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One-Electron Reduction of Aromatic Ketones by Low-Valent Lanthanides. Isolation, Structural Characterization, and Reactivity of Lanthanide Ketyl Complexes

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Abstract: In this paper we report on the isolation, structural characterization, and reactivity of a series of lanthanide ketyl complexes, which are generated by reactions of benzophenone and fluorenone with several different types of lanthanide reducing agents including $Ln(OAr)_2(L)_x$ (Ar = C_6H_2-^{t}Bu$_2$-2,6-Me-4; **1a:** Ln = Sm, L = THF, $x = 3$; **1b:** Ln = Yb, L = THF, $x = 3$; **1c:** Ln = Sm, L = HMPA, $x = 2$; **1d:** Ln = Yb, L = HMPA, $x = 2$), $(C_5Me_5)_2Ln(THF)_2$ (Ln = Sm, Yb), $(C_5Me_5)Sm(OAr)(HMPA)_2$, $Sm(N(SiMe_3)_2)_2(THF)_2$, and Ln/HMPA (Ln = Sm, Yb) (HMPA = hexamethylphosphoric triamide). Reactions of **1a**−**d** with 1 equiv of fluorenone in THF afforded the corresponding ketyl complexes $Ln(OAr)_2(ketyl)(L)_2$ (**3a**−**d**) in 85−90% isolated yields. Hydrolysis of **3a** (Ln = Sm, L = THF) gave the corresponding pinacol-coupling product, 1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diol (**4**), while air oxidation of **3a** yielded fluorenone almost quantitatively. Reaction of **3a** with 1 equiv of **1a** followed by hydrolysis afforded fluorenol quantitatively. When **3a** was dissolved in hexane/ether, pinacol-coupling of the ketyl unit occurred to give the OEt_2-coordinated pinacolate complex $[Sm(OAr)_2(OEt_2)]_2[\mu\text{-pinacolate}]$ (**5a**, pinacolate = 1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diolate). Dissolving **5a** in THF regenerated **3a** via C−C bond cleavage of the pinacolate unit, showing that the pinacol-coupling process was reversible. Addition of 2 equiv of HMPA (per Sm) to a THF solution of **3a** or **5a** gave the corresponding HMPA-coordinated ketyl complex **3c**. Complex **3c** was more stable than **3a**, and no reaction was observed when **3c** was treated similarly with hexane/ether. Reactions of fluorenone with $(C_5Me_5)_2Ln(THF)_2$ (Ln = Sm, Yb) and $(C_5Me_5)Sm(OAr)(HMPA)_2$ gave the corresponding ketyl complexes $(C_5Me_5)_2Ln(ketyl)(THF)$ (**3e**: Ln = Sm, **3f**: Ln = Yb) and $(C_5Me_5)Sm(OAr)(ketyl)(HMPA)$ (**3i**), respectively. In contrast, the similar reaction of $Sm(N(SiMe_3)_2)_2(THF)_2$ with fluorenone in THF yielded the pinacolate complex $[Sm(N(SiMe_3)_2)_2(THF)]_2[\mu\text{-pinacolate}]$ (**5b**) as the only isolable product, although the formation of a ketyl species was evident in THF solution. Reaction of 4 equiv of HMPA with **5b** in THF gave a mixture of $Sm(N(SiMe_3)_2)_2(ketyl)(HMPA)_2$ (**3k**) and $[Sm(N(SiMe_3)_2)_2(HMPA)]_2[\mu\text{-pinacolate}]$ (**5c**), while reactions of **5b** with 4 equiv of ArOH (Ar = C_6H_2-^{t}Bu$_2$-2,6-Me-4) in THF and THF/HMPA produced the corresponding ArO-ligated ketyl complexes **3a** and **3c**, respectively. A variable-temperature UV−vis spectroscopic study in toluene derived a dissociation enthalpy of 11 kcal/mol for **5b**. Reactions of metallic Ln (Ln = Sm, Yb) with 3 equiv of fluorenone and 3 equiv of HMPA in THF yielded the corresponding tris(ketyl)metal complexes $Ln(ketyl)_3(HMPA)_3$ (**7a**: Ln = Sm, **7b**: Ln = Yb). Hydrolysis of **7a,b** afforded the pinacol **4**, while reaction of **7a** with 0.5 equiv of **4** or benzopinacol produced the fluorenoxide/pinacolate complex **6**. Reaction of **4** with $Sm(N(SiMe_3)_2)_3$ in THF/HMPA also afforded **6**. In contrast to the reactions of fluorenone, the similar reactions of the above reducing agents with benzophenone did not afford a structurally characterizable ketyl species, and in the case of **1d**, the corresponding hydrogen radical abstraction product $Yb(OCHPh_2)_2(OAr)(HMPA)_2$ (**2**) was isolated.

Introduction

Ketyls, or radical anions of ketones, which are usually generated via one-electron reduction of ketones by reducing metals, are among the most important intermediates in organic chemistry.[1] These species were discovered more than 100 years ago by the use of alkali metals as reducing agents.[2] The subsequent extensive studies have shown that other reducing metals such as low-valent titanium[1c,d,g−i,l] and lanthanides[1a−b,c,e,g,i] are also good electron-transfer agents for the generation of ketyl species. It is now well-known that ketyl species as key intermediates play a very important role in a variety of reactions involving organic carbonyl groups, such as reductions,[1g,j,k,m] pinacol-couplings,[1c,d,g] olefin formations (the McMurry

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(1) For reviews on metal ketyl-involved organic synthesis, see: (a) Skrydstrup, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 345. (b) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307. (c) Wirth, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 61. (d) Fürstner, A.; Bogdanovic, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2442. (e) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29. (f) Huffman, J. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 8, Chapter 1.4. (g) Robertson, G. M. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 3, Chapter 2.6. (h) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513. (i) Kahn, B. E.; Riecke, R. T. *Chem. Rev.* **1988**, *88*, 733. (j) Pradhan, S. K. *Tetrahedron* **1986**, *42*, 6351. (k) Huffman, J. W. *Acc. Chem. Res.* **1983**, *16*, 399. (l) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405; **1974**, *7*, 281. (m) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; Chapter 3.

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reaction),[1c,d,g−i,l] cyclizations,[1a,b,e] and Grignard reactions,[3] many of which have been successfully applied to the synthesis of a variety of complicated organic compounds including natural products and strained carbocycles.

Despite these extensive applications of ketyls in organic synthesis, structural information on these highly reactive species was for a long time solely limited to the spectroscopic observations of the in-situ-generated species.[4] Attempts to isolate a ketyl species were hampered by its extremely high reactivity and instability. Reactions of $CpTiX_2$ (X = Br, Cl),[5] Cp_2TiR,[6] or $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(EtOH)_2$[7] with ketones were reported to give rapidly the corresponding pinacol-coupling products, while the putative ketyl intermediates were not observed. The use of a sterically demanding titanium(III) reductant such as $Ti(OSi^tBu_3)_3$ suppressed the pinacol-coupling reaction, but hydrogen abstraction or dimerization via $C_\alpha{-}C_{para}$ coupling of aromatic ketones took place.[4a]

The first structurally characterizable metal ketyl complex was isolated very recently in our laboratories by reaction of a bulky samarium(II) aryloxide with fluorenone.[8] Following this work, several alkali,[9] alkaline earth,[10] and lanthanide metal ketyl complexes[11] were also isolated and structurally characterized.[12,13] During these preliminary studies we noticed that the reactivity and stability of a ketyl species were somewhat metal-dependent, and lanthanide ketyls seemed to be the most reactive ketyl species among what we surveyed. These findings, together with the recent rapidly growing interest in lanthanide ketyl-mediated organic synthesis,[1a,b,e,14] promoted us to make a further detailed investigation into the formation, structures, and reactivity of lanthanide ketyls. In this paper, we report on the reactions of benzophenone and fluorenone with several different types of lanthanide reducing agents, which include $Ln(OAr)_2(L)_x$ (Ln = Sm, Yb; Ar = C_6H_2-$^tBu_2$-2,6-Me-4; L = THF (x = 3), HMPA (hexamethylphosphoric triamide, x = 2)), $(C_5Me_5)_2Ln(THF)_2$ (Ln = Sm, Yb), $(C_5Me_5)Sm(OAr)(HMPA)_2$, $Sm(N(SiMe_3)_2)_2(THF)_2$, and Ln/HMPA (Ln = Sm, Yb). We have found that the stability and reactivity of lanthanide ketyl complexes are strongly influenced by the ancillary ligands, solvents, and the structure of their parent ketones. By tuning these factors, a new series of lanthanide ketyl complexes has been isolated and structurally characterized, and unprecedented insights into the elementary steps of some of the reactions of ketyl species have been gained. A portion of this work has been previously communicated.[8,11]

Results and Discussion

Attempts To Isolate a Benzophenone Ketyl Species. Our approach to an isolable lanthanide ketyl species was initiated by reaction of a sterically demanding lanthanide reducing agent with a highly conjugated ketone. Partly due to our interest in aryloxide-stabilized lanthanide complexes,[15] the bulky lanthanide(II) aryloxides $Ln(OAr)_2(L)_x$ (Ar = C_6H_2-$^tBu_2$-2,6-Me-4; **1a:** Ln = Sm, L = THF, x = 3;[15b] **1b:** Ln = Yb, L = THF, x = 3;[16] **1c:** Ln = Sm, L = HMPA, x = 2; **1d:** Ln = Yb, L = HMPA, x = 2)[15c,e] were first chosen as our reducing agents. Reactions of **1a**−**d** with 1 equiv of benzophenone were carried out in THF at room temperature. In all these reactions addition of a Ln(II) reductant to a THF solution of benzophenone resulted in an immediate color change to blue (Ln = Yb) or purple (Ln = Sm), which was characteristic for the formation of a ketyl species. However, attempts to obtain a single crystal of a ketyl species suitable for a diffraction study were not successful. Evaporation of the solvent gave either oily or fine crystalline products.[17] When the deeply colored product solutions were left at room temperature for a long time, colorless precipitates were usually formed, which after hydrolysis yielded benzhydrol and ArOH. In the case of **1d**, colorless blocks of **2** suitable for a diffraction study were deposited from a blue THF/benzene solution after a few weeks (Scheme 1). An X-ray analysis has revealed that **2** is an Yb(III) aryloxide/diphenylmethoxide complex, $Yb(OCHPh_2)_2(OAr)(HMPA)_2$, in which the central Yb atom is five-coordinated by one ArO, two HMPA, and two diphenylmethoxy ($OCHPh_2$) ligands (Figure 1, Table 1).[18]

Complex **2** was apparently formed via hydrogen radical abstraction from the solvent by the initially generated ketyl radical species (Scheme 1). The isolation of **2** in the present reaction suggested that the corresponding benzophenone ketyl

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(2) For early examples of the formation of ketyl species, see: (a) Bechman, F.; Paul, T. *Justus Liebigs Ann. Chem.* **1891**, *266*, 1. (b) Schlenk, W.; Weichel, T. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1182. (c) Schlenk, W.; Thal, A. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 2480.

(3) For examples, see: Maruyama, K.; Katagiri, T. *J. Am. Chem. Soc.* **1986**, *108*, 6263.

(4) For examples of spectroscopic studies on metal ketyls, see: (a) Covert, K. J.; Wolczanski, P. T.; Hill, S. A.; Krusic, P. J. *Inorg. Chem.* **1992**, *31*, 66. (b) Dams, R.; Malinowski, M.; Westdorp, I.; Geise, H. Y. *J. Org. Chem.* **1982**, *47*, 248. (c) Mao, S. W.; Nakamura, K.; Hirota, N. *J. Am. Chem. Soc.* **1974**, *96*, 5341. (d) Hirota, N. *J. Am. Chem. Soc.* **1967**, *89*, 32. (e) Hirota, N.; Weissman, S. I. *J. Am. Chem. Soc.* **1964**, *86*, 2538. (f) Steinberger, N.; Fraenkel, G. K. *J. Chem. Phys.* **1964**, *40*, 723. (g) Rieger, P. H.; Fraenkel, G. K. *J. Chem. Phys.* **1962**, *37*, 2811. (h) Maki, A. H.; Geske, D. H. *J. Am. Chem. Soc.* **1961**, *83*, 1852. (i) Hirota, N.; Weissman, S. I. *J. Am. Chem. Soc.* **1960**, *82*, 4424.

(5) Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organomet. Chem.* **1971**, *50*, 145.

(6) Klei, E.; Telgen, J. H.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *209*, 297.

(7) (a) Cotton, F. A.; DeMarco, D.; Falvello, L. R.; Walton, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 7375. (b) Anderson, L. B.; Cotton, F. A.; DeMarco, D.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 4743.

(8) Hou, Z.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1995**, *117*, 4421.

(9) Hou, Z.; Fujita, A.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 2503.

(10) Hou, Z.; Jia, X.; Wakatsuki, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1292.

(11) Hou, Z.; Fujita, A.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7843.

(12) Hou, Z.; Wakatsuki, Y. *Chem. Eur. J.* **1997**, *3*, 1005.

(13) Professor Takats recently informed us that he and co-workers had succeeded in structurally characterizing a samarium(III) benzophenone ketyl complex which was stabilized by two bulky hydrotris(3,5-dimethylpyrazolyl)borate ligands. Takats, J.; et al. Manuscript in preparation. See also: Takats, J. *J. Alloys Compd.* **1997**, *249*, 51.

(14) For examples, see: (a) Molander, G. A. McWilliams, J. C.; Noll, B. C. *J. Am. Chem. Soc.* **1997**, *119*, 1265. (b) Kawatsura, M.; Dekura, F.; Shirahama, H.; Matsuda, F. *Synlett* **1996**, 373. (c) Matsuda, F. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 987. (d) Kagan, H. B. *New J. Chem.* **1990**, *14*, 453. (e) Molander, G. A.; Kenny, C. *J. Am. Chem. Soc.* **1989**, *111*, 8236. (f) Fevig, T. L.; Elliott, R. L.; Curran, D. P. *J. Am. Chem. Soc.* **1988**, *110*, 5064. (g) Fürstner, A.; Csuk, R.; Rohrer, C.; Weidmann, H. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1729. (h) Fukuzawa, S.; Nakanishi, A.; Fujinami, T.; Sakai, S. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1669. (i) Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573. (j) Tabuchi, T.; Kawamura, K.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 3889.

(15) (a) Hou, Z.; Zhang, Y.; Yoshimura, T.; Wakatsuki, Y. *Organometallics* **1997**, *16*, 2963. (b) Hou, Z.; Fujita, A.; Yoshimura, T.; Jesorka, A.; Zhang, Y.; Yamazaki, H.; Wakatsuki, Y. *Inorg. Chem.* **1996**, *35*, 7190. (c) Yoshimura, T.; Hou, Z.; Wakatsuki, Y. *Organometallics* **1995**, *14*, 5382. (d) Hou, Z.; Yoshimura, T.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1994**, *116*, 11169. (e) Hou, Z.; Yamazaki, H.; Kobayashi, K.; Fujiwara, Y.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1992**, 722.

(16) Deacon, G. B.; Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; MacKinnon, P.; Newnham, R. H. *J. Chem. Soc., Chem. Commun.* **1989**, 935.

(17) Attempts to characterize these species by NMR spectroscopy were not successful due to the presence of paramagnetic species.

(18) Complex **2** is isostructural with the previously reported Sm(III) analogue $Sm(OCHPh_2)_2(OAr)(HMPA)_2$ (Ar = C_6H_3-$^tBu_2$-2,6).[15c] The hydrogen atoms (H(1) and H(2)) of the diphenylmethoxy groups in **2** were located by the difference Fourier syntheses.

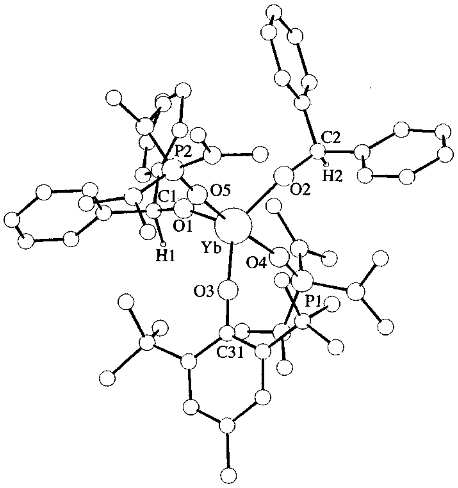

Figure 1. X-ray structure of **2**. The lattice solvent is omitted for clarity.

Scheme 1

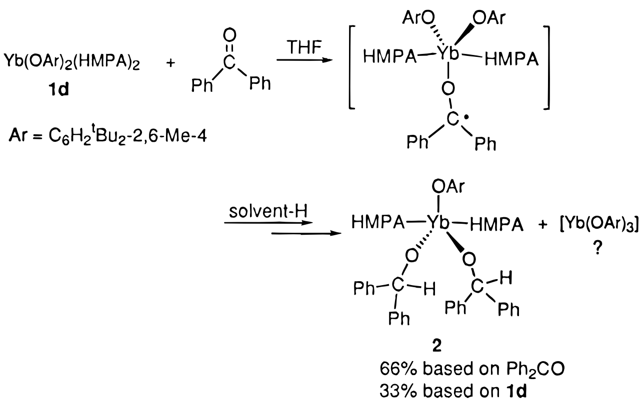

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **2**

Yb−O(1)	2.055(6)	Yb−O(2)	2.103(5)
Yb−O(3)	2.119(5)	Yb−O(4)	2.255(7)
Yb−O(5)	2.246(7)	O(1)−C(1)	1.380(11)
O(2)−C(2)	1.369(9)	O(3)−C(31)	1.322(9)
C(1)−H(1)	1.19(10)	C(2)−H(2)	1.18(10)
O(1)−Yb−O(2)	112.8(3)	O(1)−Yb−O(3)	118.2(2)
O(1)−Yb−O(4)	93.5(3)	O(1)−Yb−O(5)	94.9(3)
O(2)−Yb−O(3)	129.0(2)	O(2)−Yb−O(4)	87.2(3)
O(2)−Yb−O(5)	86.9(3)	O(3)−Yb−O(4)	88.9(3)
O(3)−Yb−O(5)	89.7(2)	O(4)−Yb−O(5)	171.2(2)
Yb−O(1)−C(1)	161.1(7)	Yb−O(2)−C(2)	146.2(6)
Yb−O(3)−C(31)	170.6(6)		

species was too reactive to survive in solution for a long time.[19] However, the lack of formation of a dimerization product in this reaction did demonstrate that the ArO ligand was able to suppress the coupling process of the resulting ketyl species.

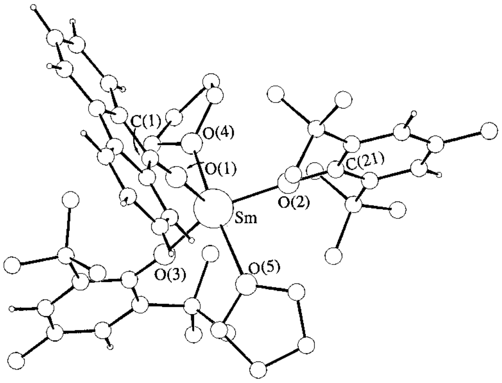

Figure 2. X-ray structure of **3a**. The lattice solvent is omitted for clarity.

Scheme 2

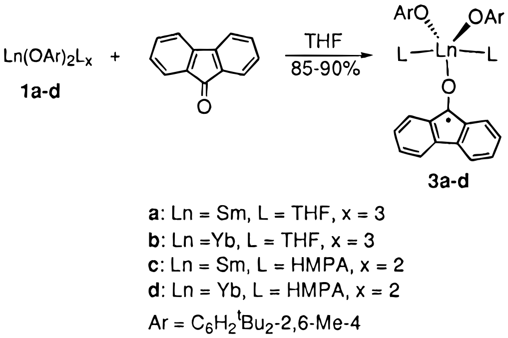

Table 2. Summary of the Selected Bond Lengths (Å) and Angles (deg) for Ln(ketyl)(OAr)$_2$(L)$_2$ (**3a:** Ln = Sm, L = THF; **3b:** Ln = Yb, L = THF; **3c**: Ln = Sm, L = HMPA)

	3a	3b	3c
Ln−O(ketyl)	2.159(4)	2.066(4)	2.20(2)
Ln−OAr	2.163(4)	2.083(4)	2.23(3)
Ln−L	2.457(4)	2.341(4)	2.35(2)
C−O(ketyl)	1.313(7)	1.309(7)	1.31(4)
Ln−O−C(ketyl)	175.2(3)	175.9(4)	165(2)
ArO−Ln−OAr	139.7(1)	141.9(2)	133.2(7)
L−Ln−L	163.2(1)	163.2(2)	177.7(7)

Fluorenone Ketyl Complexes with an Aryloxide (ArO) Ligand. To suppress the hydrogen abstraction reaction by the resulting ketyl species, a further highly conjugated ketone, fluorenone, was used to react with **1a**−**d**. In contrast to the reactions of benzophenone, all these reactions afforded the corresponding ketyl complexes (**3a**−**d**) as deeply colored crystals suitable for diffraction studies (Scheme 2). Complexes **3a**−**d** all have a similar structure in which one fluorenone ketyl and two ArO ligands are placed at the equatorial and two L (L = THF or HMPA) ligands are located at the apical positions of a distorted trigonal bipyramid (Table 2, Figure 2).[20] The C−O bond distances of the ketyl units are around 1.31 Å, which are significantly longer than those of fluorenone (1.21(3) Å)[21] and benzophenone (1.23(2) Å),[22] but shorter than that of the fluorenoxy unit in Sm(OC$_{13}$H$_9$)(OAr)$_2$(HMPA)$_2$ (1.404(10) Å) (Ar = C$_6$H$_3$-^{t}Bu$_2$-2,6).[15c] Similar to other metal fluorenone ketyl complexes,[9,12] the radical carbon atom in each ketyl unit is still in an sp^2-hybrid state and the oxygen atom is within the same plane as the fluorenyl ring.

Reflecting the typical reactivity of a ketyl species, hydrolysis of **3a** gave the corresponding pinacol-coupling product **4**,[23] while air oxidation of **3a** yielded fluorenone almost quantitatively (Scheme 3). Reaction of **3a** with 1 equiv of **1a** produced a

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(19) Reactions of (C$_5$Me$_5$)$_2$Ln(THF)$_2$ (Ln = Sm, Yb) with benzophenone in THF did not give a structurally characterizable benzophenone ketyl complex either, which yielded light-yellow precipitates after a few weeks.

(20) In the case of **3d**, some methyl groups in the HMPA ligands could not be well refined due to the poor quality of the crystal. However, the connectivity of the whole molecule was unequivocally determined. Crystal data for **3d**: $C_{110}H_{180}N_{12}O_{10}P_4Yb_2$, FW = 2300.71, orthorhombic, space group $I2_12_12_1$ (no. 24), $a = 29.476(8)$ Å, $b = 29.487(9)$ Å, $c = 13.831(4)$ Å, $V = 12021(6)$ Å^3, $Z = 4$, $D_c = 1.27$ g cm^{-3}, $R = 0.0888$, $Rw = 0.105$. There were two independent molecules in the unit cell, each of which had a crystallographic C_2 axis passing through the Yb and the oxygen and carbon atoms of the CO group of the ketyl unit.

(21) Hou. Z.; Fujita, A.; Yamazaki, H.; Wakatsuki. Y. unpublished result.

(22) Fleischer, E. B.; Sung, N.; Hawkinson, S. *J. Phys. Chem.* **1968**, *72*, 4311.

Scheme 3

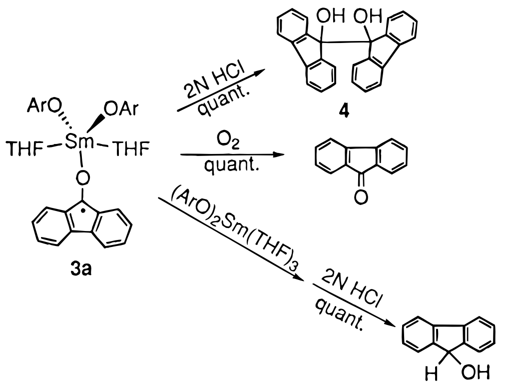

Table 3. Summary of the UV−Vis Data for Lanthanide Ketyl Complexes[a]

	λ/nm ($\epsilon \times 10^{-3}$ cm^{-1} M^{-1})
3a	440 (1.7), 416 (1.4)
3b	440 (2.0), 416 (1.8)
3c	443 (2.5), 419 (1.4)
3d	441 (1.9), 417 (1.3)
3e	443 (4.1), 420 (3.3)
3f	442 (3.7), 419 (2.9)
3g	444 (4.8), 420 (3.5)
3h	443 (4.7), 420 (3.4)
3i	442 (3.3), 416 (2.5)
3j[b]	442 (2.0), 419 (1.4)
3k[c]	442 (2.2), 417 (1.4)
7a	445 (3.7), 423 (1.9)
7b	445 (4.4), 420 (2.1)

[a] In THF, at room temperature. [b] Generated by dissolving **5b** in THF. [c] Generated by dissolving **5b** in THF with 4 equiv of HMPA.

THF-insoluble purple precipitate which upon hydrolysis afforded fluorenol quantitatively, suggesting that a fluorenone dianion intermediate was formed.[15c−e,23]

An X-band ESR spectrum was not observed for any of **3a**−**d** at either room temperature or −196 °C, probably owing to the antiferromagnetic superexchange interaction between the ketyl radical and the lanthanide(III) spins and/or the spin−lattice relaxation of the ketyl radical via the paramagnetic lanthanide(III) ions.[24] The UV−vis spectra of **3a**−**d** in THF were generally similar to each other (Table 3), and comparable with those for the in situ generated fluorenone ketyl species.[4] In the case of the THF-coordinated complexes **3a**,**b**, a broad absorption at 500−640 nm was also observed in addition to the relatively sharp absorptions around 440 and 416 nm. Interestingly, when **3a**,**b** were dissolved into hexane, the intensity of the absorption spectra dropped dramatically along with a visible color fading. Upon evaporation of the hexane solvent, pale yellow powders were obtained. In the case of **3a**, recrystallization of the pale yellow powder from hexane with a small amount of diethyl ether afforded light yellow crystals of **5a** (Scheme 4). An X-ray analysis has shown that **5a** is a binuclear samarium(III)−pinacolate complex formed by dimerization of the ketyl **3a** at the radical carbon and simultaneous replacement of the two THF ligands with one Et_2O (Figure 3, Table 4). A crystallographic inversion center exists on the newly formed C(1)−C(1′) bond. This C−C bond (1.613(9) Å) is significantly longer than a typical covalent C−C single bond (1.54 Å),[25] and also longer than those found in its parent pinacol, **4** (1.57(1) Å).[26] Reflecting this very long bond distance, the C(1)−C(1′) bond in **5a** was very weak and could be easily broken to regenerate the ketyl **3a** by addition of a strongly coordinative solvent. The light yellow pinacolate **5a** turned immediately to purple brown upon addition of THF, and **3a** was quantitatively recovered from this THF solution (Scheme 4), which unequivocally demonstrated that the pinacol-coupling of **3a** to give **5a** was reversible. Addition of 2 equiv of HMPA (per Sm) to a THF solution of **3a** or **5a** gave almost quantitatively the corresponding HMPA-coordinated ketyl complex **3c** (Scheme 4). Since the coordination ability of HMPA is much stronger than that of THF,[27] complex **3c** was much

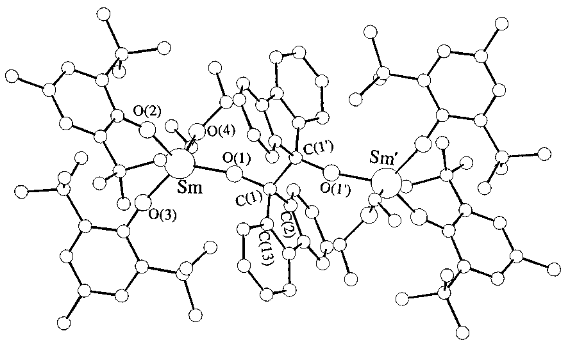

Figure 3. X-ray structure of **5a**. The lattice solvent is omitted for clarity.

Scheme 4

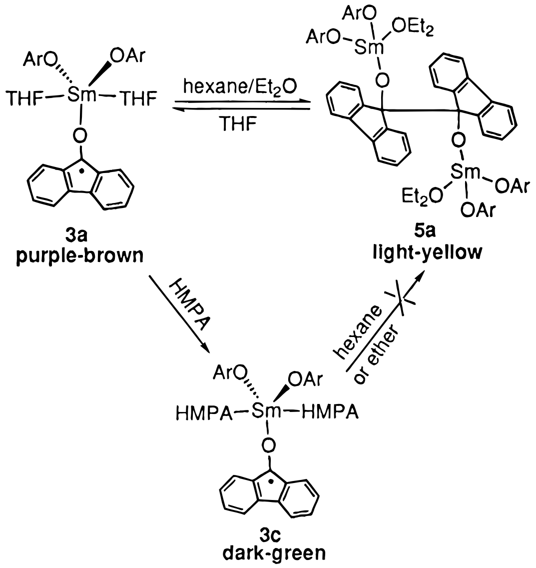

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **5a**

Sm−O(1)	2.099(4)	Sm−O(2)	2.115(3)
Sm−O(3)	2.141(5)	Sm−O(4)	2.435(5)
C(1)−O(1)	1.401(7)	C(1)−C(1′)	1.613(9)
Sm(1)−O(1)−C(1)	165.9(4)	O(1)−Sm(1)−O(2)	112.4(2)
O(1)−Sm(1)−O(3)	127.2(2)	O(1)−Sm(1)−O(4)	98.0(2)
O(2)−Sm(1)−O(3)	108.9(2)	O(3)−Sm(1)−O(4)	94.6(2)

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(23) (a) Hou, Z.; Yamazaki, H.; Fujiwara, Y.; Taniguchi, H. *Organometallics* **1992**, *11*, 2711. (b) Hou, Z.; Takamine, K.; Aoki, O.; Shiraishi, H.; Fujiwara, Y.; Taniguchi, H. *J. Org. Chem.* **1988**, *53*, 6077.

(24) (a) Anderson, P. W. In *Magnetism*; Rado, G. T., Suhl, H., Eds.; Academic Press: New York, 1963; Vol. I, Chapter 2. (b) Manenkov, A. A.; Orbach, R. *Spin−Lattice Relaxation in Ionic Solids*; Harper & Row: New York, 1966.

(25) For a recent overview on overlong C−C single bonds see: Kaupp, G.; Boy, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 48.

(26) Single crystals of the pinacol **4** crystallized in the form of $[\mathbf{4}]_2\cdot OEt_2$ from ether/hexane. Crystal data: $C_{42}H_{46}O_5$, FW = 798.99, triclinic, space group $P\bar{1}$ (no. 2), a = 8.732(4) Å, b = 14.309(2) Å, c = 17.593(3) Å, α = 94.25(1)°, β = 99.79(2)°, γ = 87.37(2)°, V = 2159(1) Å^3, Z = 2, D_c = 1.23 g cm^{-3}, R = 0.0716, Rw = 0.0945. Details will be reported elsewhere.

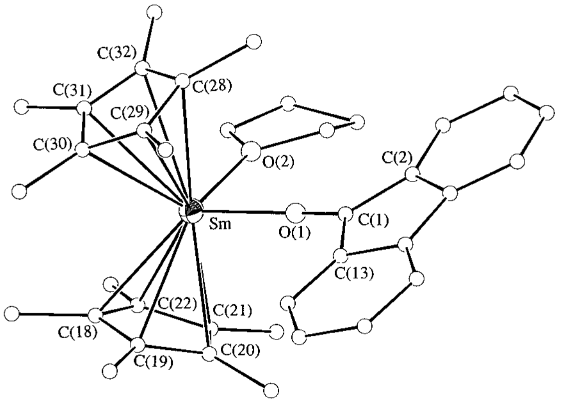
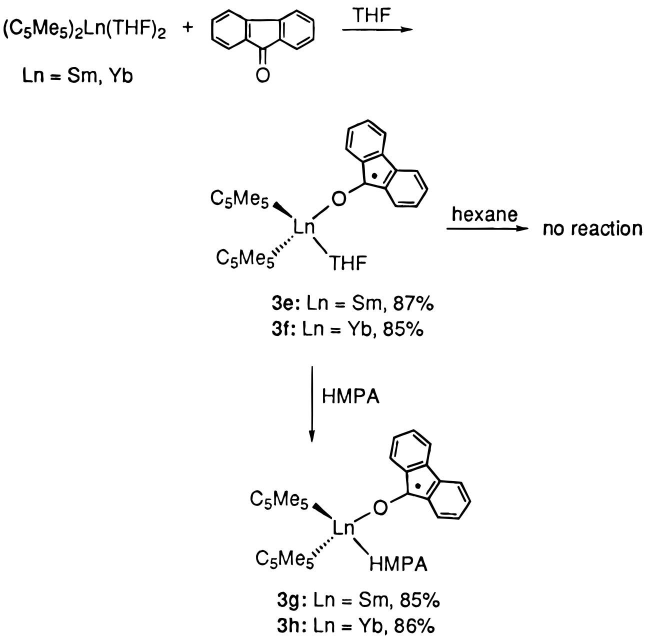


Figure 4. X-ray structure of **3e**.

Scheme 5



more stable than **3a**, and no change was observed when **3c** was treated similarly with hexane/ether. These results clearly demonstrated that the stability and reactivity of a ketyl species were strongly influenced by the ancillary ligands bound to the central metal, which thus promoted a further study on ketyl complexes bearing other ancillary ligands.

Fluorenone Ketyl Complexes with a C_5Me_5 Ligand. Reactions of $(C_5Me_5)_2Ln(THF)_2$ (Ln = Sm,[28] Yb[29]) with 1 equiv of fluorenone in THF were carried out similarly, and the corresponding ketyl complexes **3e,f** were isolated (Scheme 5). An X-ray analysis has shown that **3e** possesses a distorted tetrahedral structure in which the central Sm atom is surrounded by one ketyl, one THF, and two C_5Me_5 ligands (Figure 4, Table 5). Although a single crystal of **3f** suitable for a diffraction study was not obtained, its HMPA analogue, **3h**, which was isolated by reaction of **3f** with 1 equiv of HMPA in THF (Scheme 5), was successfully characterized by an X-ray analysis (Figure 5, Table 5).

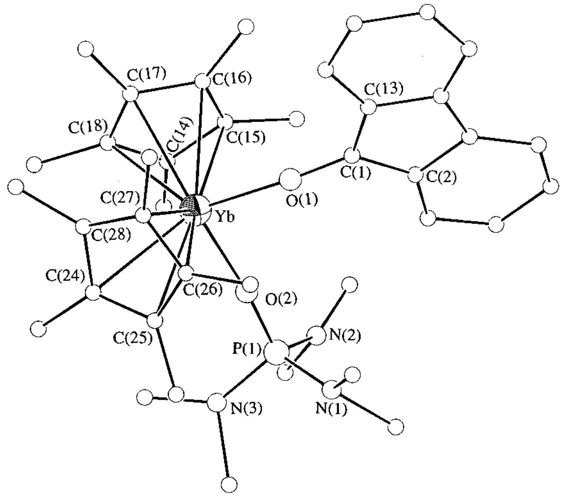
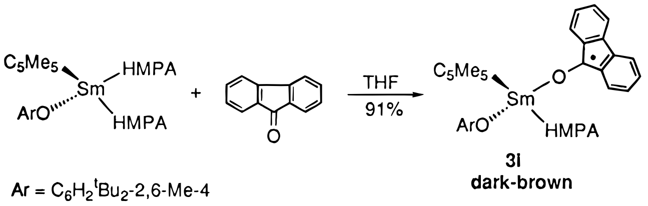


Figure 5. X-ray structure of **3h**. The lattice solvent is omitted for clarity.

Table 5. Summary of the Selected Bond Lengths (Å) and Angles (deg) for $(C_5Me_5)_2Ln(ketyl)(L)$ (**3e:** Ln = Sm, L = THF; **3h:** Ln = Yb, L = HMPA) and $(C_5Me_5)(ArO)Ln(ketyl)(L)$ (**3i:** Ln = Sm, L = HMPA)

	3e	3h	3i
Ln−O(ketyl)	2.234(7)	2.108(7)	2.200(7)
Ln−Cp*(av.)	2.724(12)	2.675(12)	2.729(10)
Ln−OAr			2.158(6)
Ln−L	2.519(8)	2.268(8)	2.295(6)
C−O(ketyl)	1.317(11)	1.312(13)	1.309(13)
Ln−O−C(ketyl)	164.3(6)	169.1(8)	171.4(7)
Cp*(centroid)−Ln−Cp*-(centroid)	136.1(3)	132.5(5)	
Cp*(centroid)−Ln−OAr			120.4(3)
O(ketyl)−Ln−L	91.6(2)	93.0(8)	94.7(3)
O(ketyl)−Ln−Cp*-(centroid)	111.5(2), 102.5(2)	104.8(6), 105.5(6)	111.7(3)
O(ketyl)−Ln−OAr			113.4(3)
L−Ln−Cp*(centroid)	104.4(2), 101.5(4)	105.3(6), 108.7(5)	109.8(3)
L−Ln−OAr			103.2(3)

Scheme 6



In contrast to the ArO-ligated ketyl complexes **3a−d** which required two THF or HMPA ligands as an additional stabilizing moiety, the C_5Me_5-ligated complexes **3e−h** needed only one THF or HMPA ligand. This difference apparently resulted from the larger bulkiness of C_5Me_5 as compared to that of the ArO ligand. Addition of hexane/ether to the THF-coordinated **3e,f** did not cause any further reaction, showing that the C_5Me_5-supported **3e,f** were more stable and less reactive than the ArO-supported **3a,b**.

The similar reaction of $(C_5Me_5)Sm(OAr)(HMPA)_2$[15a] with fluorenone also gave the corresponding ketyl complex **3i** (Scheme 6, Figure 6, Table 5), demonstrating that the heteroleptic C_5Me_5/OAr ligand set was also able to stabilize a ketyl species. It is also noteworthy that although the homoleptic analogues **3c,g** were isolable, ligand redistribution of **3i** to give either of these complexes was not observed. Complex **3i**

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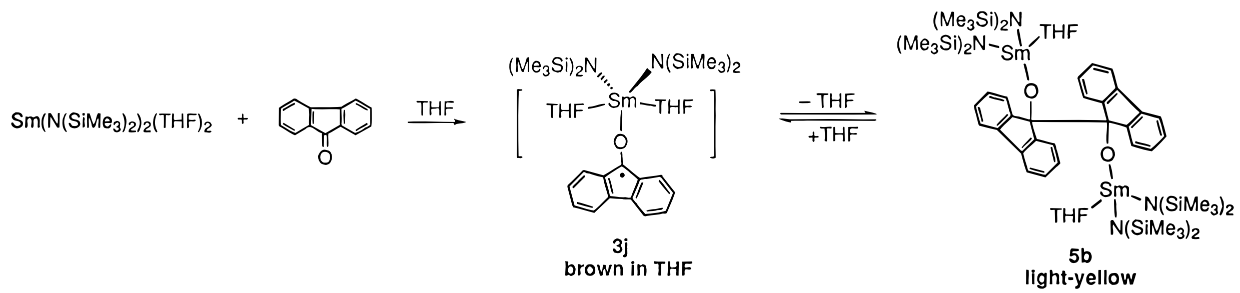
[27] (a) Hou, Z.; Zhang, Y.; Wakatsuki, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 149. (b) Hou, Z.; Wakatsuki, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1205.

[28] Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter; W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941.

[29] (a) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652. (b) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A. *Inorg. Chem.* **1980**, *19*, 2999.

Scheme 7



3j
brown in THF

5b
light-yellow

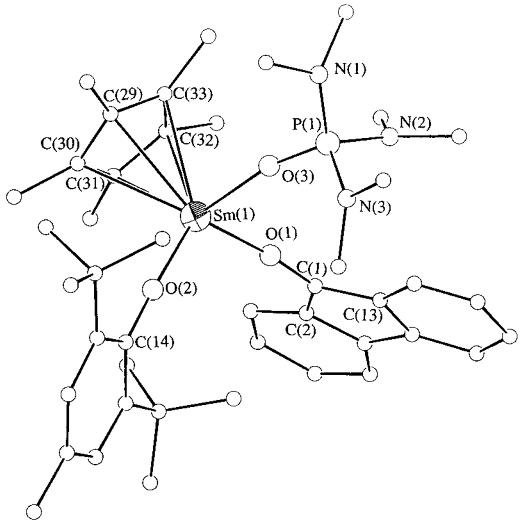


Figure 6. X-ray structure of **3i**.

represents a rare example of a lanthanide complex which bears all different ligands.

Fluorenone Ketyl Complexes with an N(SiMe$_3$)$_2$ Ligand. Reaction of Sm(N(SiMe$_3$)$_2$)$_2$(THF)$_2$[30] with 1 equiv of fluorenone in THF yielded a brown solution whose UV−vis spectrum was almost identical with that of **3a** in THF (Table 3), suggesting that the corresponding ketyl species like **3j** was formed. Slow concentration of the brown THF solution, however, yielded light yellow crystals of the pinacolate complex **5b** (Scheme 7). An X-ray analysis has shown that the overall structure of **5b** is similar to that of the ArO-supported pinacolate **5a**. Each Sm atom is four-coordinated by two N(SiMe$_3$)$_2$, one THF, and half of a pinacolate unit, and a crystallographic inversion center exists on the central C−C bond of the pinacolate unit (Figure 7).[31] Complex **5b** was soluble and ^{1}H NMR detectable in C$_6$D$_6$. The fluorenyl units showed broad multiplets at δ 7.30−8.30, while the N(SiMe$_3$)$_2$ groups appeared as a broad singlet at δ −2.25. The THF ligands gave two broad singlets at δ 2.85 and −1.31, respectively. Ligand redistribution of **5b** to give the known Sm(N(SiMe$_3$)$_2$)$_3$[32] was not observed, which was in contrast to what was observed in the reaction of Sm(N(SiMe$_3$)$_2$)$_2$(THF)$_2$ with CO.[30]

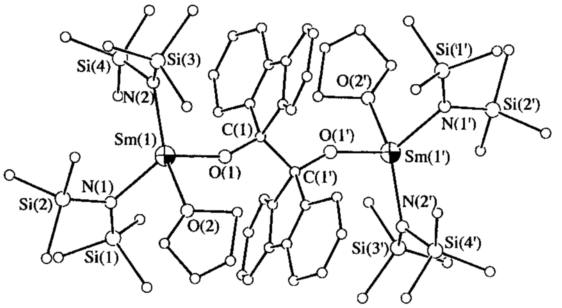


Figure 7. X-ray structure of **5b**.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **3k**

Sm(1)−O(1)	2.191(12)	Sm(1)−O(2)	2.384(13)
Sm(1)−N(1)	2.349(11)	Sm(1)−N(2)	2.313(14)
C(1)−O(1)	1.34(3)		
Sm(1)−O(1)−C(1)	160(2)	O(1)−Sm(1)−O(2)	85.0(6)
O(1)−Sm(1)−O(3)	85.8(6)	O(1)−Sm(1)−N(1)	114.8(6)
O(1)−Sm(1)−N(2)	114.2(6)	O(2)−Sm(1)−O(3)	169.9(4)
O(2)−Sm(1)−N(1)	91.7(5)	O(2)−Sm(1)−N(2)	92.4(5)
O(3)−Sm(1)−N(1)	96.1(5)	O(3)−Sm(1)−N(2)	87.3(5)
N(1)−Sm(1)−N(2)	131.0(5)		

Attempts to isolate a ketyl species such as **3j** from THF were unsuccessful and always resulted in the formation of the pinacolate **5b**, which was in sharp contrast to the case of the ArO-ligated ketyl complex **3a** (see also Schemes 2 and 4). This difference probably resulted from the difference in electron-donating ability between N(SiMe$_3$)$_2$ and the ArO ligand. Since N(SiMe$_3$)$_2$ is more electron-donating than the ArO ligand, dissociation of a THF ligand from the central Sm atom in **3j** would be easier than that in **3a**, which thus causes pinacol-coupling of the ketyl radical in **3j** to occur more facilely. Nevertheless, similar to the ArO-supported pinacolate complex **5a**, the central C−C bond in **5b** could also be cleaved by addition of a strongly coordinative solvent. Dissolving the light yellow **5b** in THF gave immediately a brown solution whose UV−vis spectrum was the same as that of the solution originally obtained by the reaction of Sm(N(SiMe$_3$)$_2$)$_2$(THF)$_2$ with fluorenone in THF (Scheme 7). Addition of 4 equiv of HMPA to this THF solution afforded green-brown crystals of **3k** together with light-yellow crystals of **5c** (Scheme 8). Although a complete separation of **3k** from **5c** was difficult, single crystals of both complexes suitable for diffraction studies were successfully selected under a microscope. It has been revealed that **3k**, analogous to **3a,c**, is a fluorenone ketyl complex which is stabilized by two N(SiMe$_3$)$_2$ and two HMPA ligands (Figure 8, Table 6), while **5c**, analogous to **5a,b**, is a pinacolate complex in which each Sm atom is bound to two N(SiMe$_3$)$_2$, one HMPA, and half of a pinacolate unit (Figure 9, Table 7). The central C−C bond in **5c** (1.604(10) Å) is comparable with that in **5a** (1.613(9) Å), and longer than that of a typical covalent C−C single bond (1.54 Å),[25] showing that this C−C bond is also very weak.

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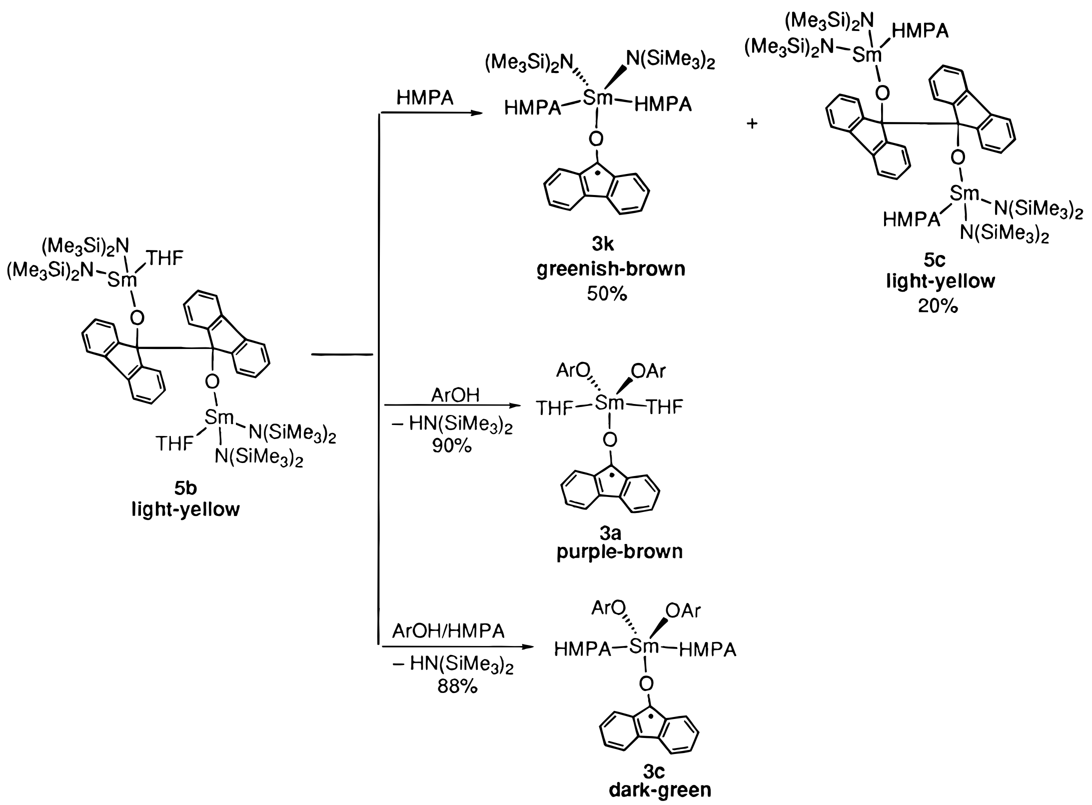
(30) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575.

(31) Since the quality of the diffraction data for **5b** was not good enough, a further structural comparison was not allowed, although the connectivity of the whole molecule could be unequivocally determined. Crystal data for **5b**: C$_{58}$H$_{104}$N$_4$O$_4$Si$_8$Sm$_2$, FW = 1446.98, monoclinic, space group $P2_1/n$ (no. 14), a = 11.624(3) Å, b = 30.648(7) Å, c = 10.971(3) Å, β = 113.08(2)°, V = 3596(2) Å^3, Z = 2, D_c = 1.34 g cm^{-3}.

(32) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J Chem. Soc., Dalton Trans.* **1973**, 1021.

Scheme 8



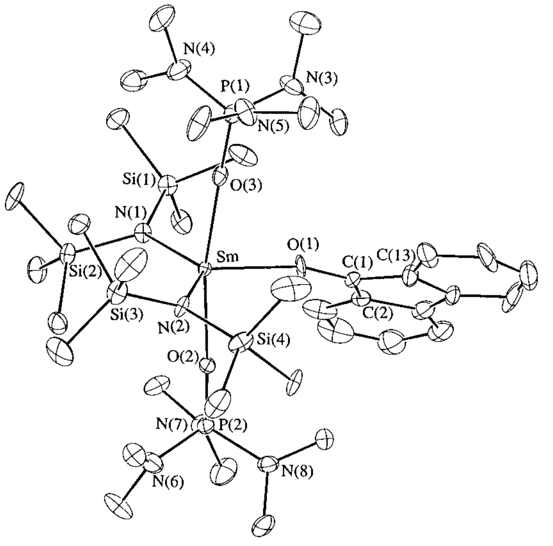


Figure 8. X-ray structure of **3k**.

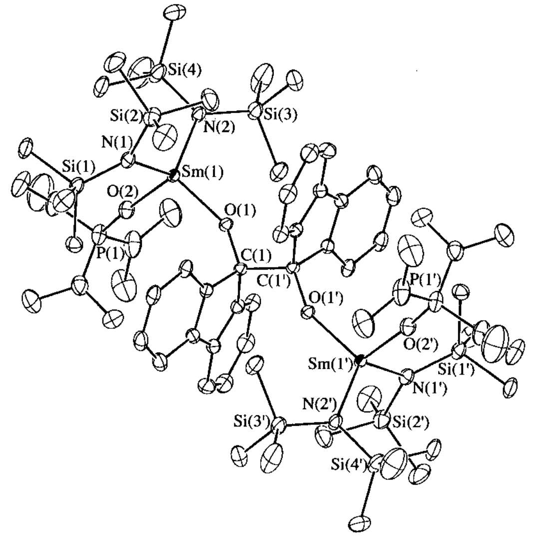


Figure 9. X-ray structure of **5c**.

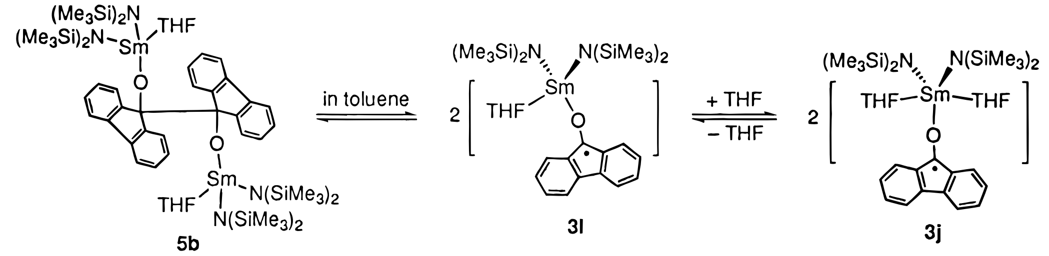
The isolation of the mono(HMPA)-coordinated pinacolate complex **5c** together with the bis(HMPA)-coordinated ketyl complex **3k** in the reaction of **5b** or **3j** with HMPA contrasts sharply with the reaction of **5a** or **3a** with HMPA, in which only the bis(HMPA)-coordinated ketyl complex **3c** was isolated (see Scheme 4), and again demonstrates that the electron-donating ability of $N(SiMe_3)_2$ is much stronger than that of the ArO ligand, and even the very strongly coordinative HMPA ligand[27] could be easily dissociated from the central Sm atom to cause pinacol-coupling of the ketyl radical in **3k**. When 4 equiv of ArOH was added to a THF solution of **5b**, proton abstraction from ArOH by the $N(SiMe_3)_2$ ligands took place and the corresponding ArO-ligated ketyl complex **3a** was isolated in 90% yield (Scheme 8). The similar reaction of **5b** with ArOH in THF/HMPA yielded selectively the corresponding bis(HMPA)-coordinated ketyl complex **3c** (Scheme 8).

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **5c**

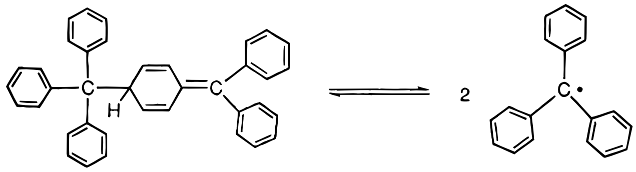
Sm(1)–O(1)	2.124(5)	Sm(1)–O(2)	2.299(7)
Sm(1)–N(1)	2.361(7)	Sm(1)–N(2)	2.332(7)
O(1)–C(1)	1.399(8)	C(1)–C(1′)	1.604(11)
Sm(1)–O(1)–C(1)	152.1(5)	O(1)–Sm(1)–O(2)	108.2(2)
O(1)–Sm(1)–N(1)	107.9(2)	O(1)–Sm(1)–N(2)	114.9(3)
O(2)–Sm(1)–N(1)	108.6(3)	O(2)–Sm(1)–N(2)	94.7(3)
N(1)–Sm(1)–N(2)	120.9(3)		

To gain more information on the C–C bond cleavage of the pinacolate **5b**, the dissociation enthalpy for **5b** was measured in toluene. Assuming that the molar absorptivity of the ketyl species **3j** generated by reaction of $Sm(N(SiMe_3)_2)_2(THF)_2$ with

Scheme 9



Scheme 10



fluorenone in THF ($\epsilon = 2.0 \times 10^3$ M^{-1} cm^{-1}) was the same as that of the mono(THF)-coordinated ketyl species **3l** (Scheme 9), the equilibrium concentrations of **3l** and **5b** in toluene were determined over a temperature range of 0−50 °C. A dissociation enthalpy of $\Delta H_{\mathrm{diss}} = 11$ kcal/mol for **5b** to give **3l** was obtained from the van't Hoff equation. This ΔH_{diss} value is much smaller than that reported for the silicon benzopinacolate ($Me_3SiOC(Ph)_2C(Ph)_2OSiMe_3$ (31 kcal/mol),[33] but comparable with that reported for the C_α−C_{para} bonds in the trityl dimer $[Ph_3C]_2$ (11−12 kcal/mol) (Scheme 10)[34] and that for the dimeric titanium(IV) alkoxide/enolate complex $[(^tBu_3SiO)_3TiOCPh_2)]_2$ (18 kcal/mol).[4a] Obviously, the dissociation enthalpy for **5b** to give the bis(THF)-coordinated ketyl complex **3j** should be much smaller than this value, since this process is accompanied by the formation of two new Sm(III)−THF bonds (Scheme 9). Since the bond energy of a Sm(II)−THF bond in $(C_5Me_5)_2Sm(THF)_n$ ($n = 1$ or 2) was found to be about 5−7 kcal/mol,[35] and a Sm(III)−THF bond is generally stronger than a Sm(II)−THF bond, the formation of two Sm(III)−THF bonds in the course of the transformation of **5b** to **3j** would release more than 10 kcal/mol, which could well compensate the enthalpy (11 kcal/mol) for the cleavage of the central C−C bond in **5b**. It is thus not difficult to understand that when a large excess amount of THF is present (e.g., in THF solution), the equilibria in Scheme 9 will be greatly shifted to the right side, and a complete dissociation of **5b** to **3j** will be easily achieved.

Lanthanide Complexes Bearing Three Independent Ketyl Ligands. Since a pinacolate complex like **5b** could be easily dissociated to the corresponding ketyl species by addition of THF or HMPA, synthesis of a samarium ketyl complex by deprotonation of the pinacol **4** with $Sm(N(SiMe_3)_2)_3$[32] in THF/HMPA was attempted. We thought that if the three $N(SiMe_3)_2$ ligands in $Sm(N(SiMe_3)_2)_3$ were all substituted by **4** through proton exchange and the central C−C bonds of the resulting pinacolate units were subsequently cleaved, formation of a Sm(III) complex bearing three independent ketyl ligands might be achieved.[9] Reaction of $Sm(N(SiMe_3)_2)_3$ with 1.5 equiv of **4** in THF was carried out in the presence of 3 equiv of HMPA (Scheme 11). A dark-green solution was formed immediately, which suggested the formation of a ketyl species. However, this dark-green solution gradually faded overnight, and a light-yellow crystalline product **6** was isolated in about 30% yield (based on Sm) (Scheme 11). When 2 equiv of **4** was used in this reaction, the yield of **6** increased to 82%. The formation of fluorenone in these reactions was also confirmed. An X-ray analysis has revealed that **6** is a dimeric samarium(III) fluorenoxide/pinacolate complex, rather than a tris(ketyl) complex (Figure 10, Table 8). A crystallographic inversion center is present at the center of the molecule. The central C−C bond distances of the pinacolate units (1.56(3) Å) are significantly shorter than those in **5a** (1.613(9) Å) and **5c** (1.604(10) Å), but comparable with that of its parent pinacol **4** (1.57(1) Å)[26] and those of the previously reported titanium[36] and tungsten[7] pinacolate complexes (1.56−1.58 Å). Consistent with this normal bond length, cleavage of the pinacolate C−C bonds in **6** to yield a ketyl species was not observed when **6** was dissolved in THF.

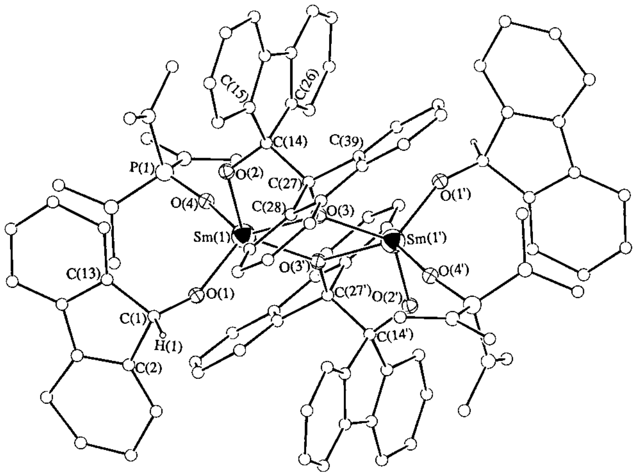


Figure 10. X-ray structure of **6**.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for **6**

Sm(1)−O(1)	2.108(14)	Sm(1)−O(2)	2.181(11)
Sm(1)−O(3)	2.371(11)	Sm(1)−O(3′)	2.293(10)
Sm(1)−O(4)	2.293(15)	C(1)−O(1)	1.39(3)
C(1)−O(1)	1.39(3)	C(14)−O(2)	1.39(2)
C(27)−O(3)	1.44(2)	C(14)−C(27)	1.56(3)
Sm(1)−O(1)−C(1)	156.0(15)	Sm(1)−O(2)−C(14)	121.1(10)
Sm(1)−O(3)−C(27)	114.4(9)	Sm(1′)−O(3)−C(27)	133.4(10)
O(1)−Sm(1)−O(2)	102.2(5)	O(1)−Sm(1)−O(3)	115.1(5)
O(1)−Sm(1)−O(3′)	116.3(5)	O(1)−Sm(1)−O(4)	110.7(6)
O(2)−Sm(1)−O(3)	70.1(4)	O(2)−Sm(1)−O(3′)	132.6(4)
O(2)−Sm(1)−O(4)	97.4(5)	O(3)−Sm(1)−O(3′)	69.2(4)
O(3)−Sm(1)−O(4)	134.1(5)	O(3′)−Sm(1)−O(4)	93.9(5)
Sm(1)−O(3)-Sm(1′)	110.8(4)		

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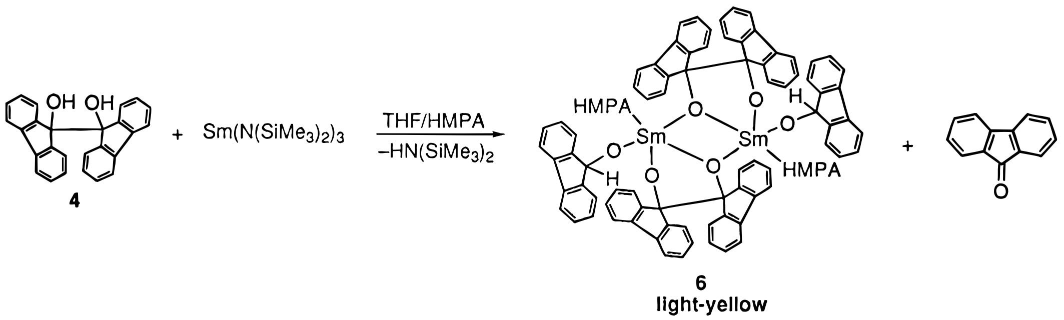
(33) (a) Newmann, W. P.; Schroeder, B.; Ziebarth, M. *Liebigs Ann. Chem.* **1975**, 2279. (b) Ziebarth, M.; Newmann, W. P. *Liebigs Ann. Chem.* **1978**, 1765.

(34) (a) Neumann, W. P.; Uzick, W.; Zarkadis, A. K. *J. Am. Chem. Soc.* **1986**, *108*, 3762. (b) Gomberg, M. *J. Am. Chem. Soc.* **1900**, *22*, 757. (c) Sholle, V. D.; Rozantsev, E. G. *Russ. Chem. Rev.* (*Engl. Trans.*) **1973**, *42*, 1011. See also ref 4a.

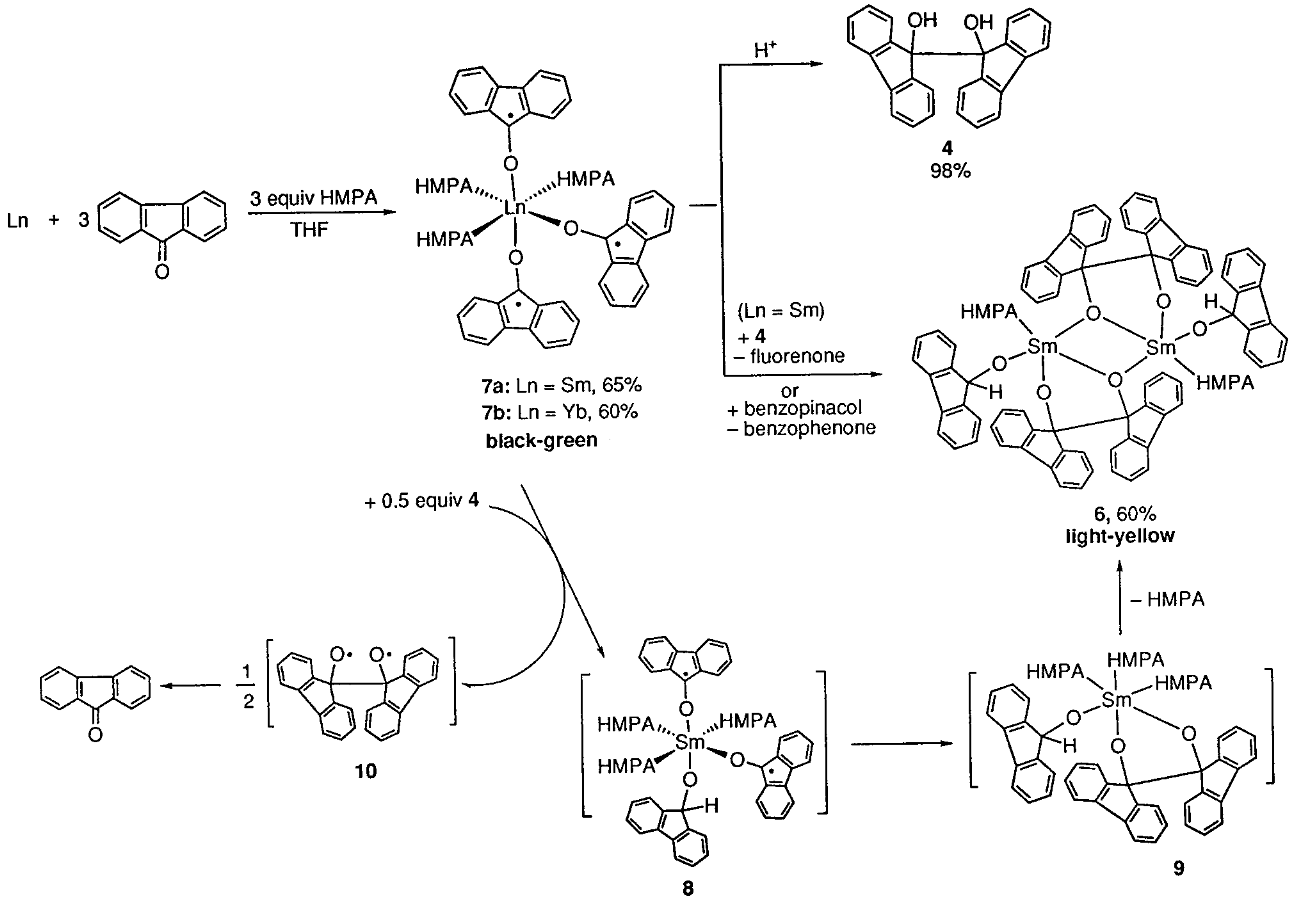
(35) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844.

(36) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

Scheme 11



Scheme 12



The fluorenoxy units in **6** were apparently formed through hydrogen abstraction by a ketyl radical species generated via C−C bond cleavage of a pinacolate unit, while the pinacolate parts in **6** could be accessed by two different possible paths. Although the direct substitution of two $N(SiMe_3)_2$ ligands in $Sm(N(SiMe_3)_2)_3$ by one molecule of **4** could be a straightforward path, intramolecular pinacol-coupling of two in situ generated ketyl species could not be ruled out (vide infra). In any event, the isolation of **6** rather than a ketyl species in the present reaction was in sharp contrast to the previously reported reaction of $NaN(SiMe_3)_2$ with **4**, in which only the corresponding sodium ketyl complex was isolated selectively.[9] These results demonstrate that the stability and reactivity of a ketyl species are metal-dependent.[12]

Parallel to the deprotonation approach to a tris(ketyl)-samarium(III) complex, reaction of Sm metal with 3 equiv of fluorenone in THF/HMPA was carried out (Scheme 12).[11,37] From this reaction dark-green blocks of **7a** were isolated in 65% yield. An X-ray analysis has shown that **7a** is a samarium(III) tris(fluorenone ketyl) complex, in which the central Sm atom is bonded in *mer*-type fashion by three ketyls and three HMPA ligands in an octahedral form (Figure 11, Table 9). The C−O bond distances in **7a** (av 1.30(2) Å) are comparable with those of the ketyl species found in **3a−c,e,h,i** (1.31−1.32 Å), and each ketyl unit also possesses a nearly planar configuration. The two mutually *trans* ketyl planes (O(2)−ketyl and O(3)−ketyl) form a relatively small dihedral angle of 8°, while the dihedral angles formed by the *cis* ketyl planes are almost half of a right angle (O(1)−ketyl/O(2)−ketyl: 49°, O(1)−ketyl/O(3)−ketyl: 43°). In contrast to the ESR-silent mono(ketyl) complexes **3a−k**, complex **7a** showed an ESR signal with $g = 2.0027$ at a temperature range of +22 to −170 °C. The similar reaction of Yb with 3 equiv of fluorenone afforded the corresponding Yb(III) tris(ketyl) complex **7b** (Scheme 12), which was isostructural and isomorphous with **7a** (Table 9).

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(37) If HMPA was not used, only a THF-insoluble yellow precipitate was obtained.

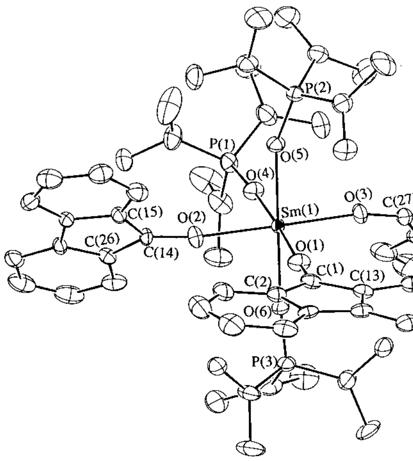

Figure 11. X-ray structure of **7a**.

Table 9. Summary of Selected Bond Lengths (Å) and Angles (deg) for Ln(ketyl)$_3$((hmpa)$_3$ (**7a:** Ln = Sm; **7b:** Ln = Yb)

	7a	**7b**
Ln−O(Ketyl)	2.234(9)	2.137(8)
Ln−O(HMPA)	2.354(8)	2.250(7)
C−O	1.30(2)	1.30(1)
Ln-O−C	170.8(8)	170.9(8)

Hydrolysis of **7a,b** gave almost quantitatively the corresponding pinacol **4** (Scheme 12).[23] Interestingly, the reaction of **7a** with 0.5 equiv of **4** afforded **6** and fluorenone (Scheme 12). Although the formation of **6** from **7a** might formally be viewed as hydrogen radical addition to one ketyl and pinacolate substitution of the other two ketyls in **7a**, a further study showed that this was not the case. Reaction of **7a** with benzopinacol also gave **6**, and in this reaction the formation of benzophenone instead of fluorenone was confirmed (Scheme 12). These results strongly suggested that the formation of **6** was via hydrogen radical abstraction from the pinacol by one ketyl, followed by pinacol-coupling of the other two ketyls together with simultaneous release of two HMPA ligands in **7a** (Scheme 12). Homolytic C−C bond cleavage of the biradical species (e.g., **10**), which was formed by dehydrogenation (−H$^\bullet$) of the pinacol, would afford the corresponding ketone. It is noteworthy that the small steric change, which was caused by the transformation of one of the three fluorenone ketyls to a fluorenoxy unit, imposed crucial influence on the stability and reactivity of the other two ketyls.

Concluding Remarks

The results described above have demonstrated that the stability and reactivity of a ketyl species are extremely susceptible to the steric environment around the central metal ion. Both anionic and neutral (solvent) ligands play an important role in determining the behavior of a ketyl species. The sterically demanding bis(pentamethylcyclopentadienyl) ligand set $(C_5Me_5)_2$ together with a neutral L (L = THF or HMPA) ligand offers a good stabilizing environment for a lanthanide fluorenone ketyl species, while the less bulky $(ArO)_2$ or $((Me_3Si)_2N)_2$ ligand set requires two L (L = THF or HMPA) ligands for the stabilization of the same ketyl species. In the latter case, dissociation of one of the two L ligands from the central metal ion easily occurs to cause pinacol-coupling of the ketyl, and this takes place more facilely for the $(Me_3Si)_2N$-ligated complexes than for the ArO-ligated ones, due to the stronger electron-donating ability of $N(SiMe_3)_2$. Recoordination of an L ligand to the metal atom of the resulting pinacolate easily cleaves the central C−C bond and regenerates the ketyl, which thus makes the pinacol-coupling process reversible. The relatively small dissociation enthalpy for the pinacolate complexes (e.g., $\Delta H_{diss} = 11$ kcal/mol for **5b**) could well account for this reversibility. HMPA as a neutral and strongly coordinative ligand offers an excellent stabilizing moiety for both mono- and multi-ketyl complexes. The transformation of the tris(ketyl) complex **7a** to the fluorenoxide/pinacolate complex **6** provides unprecedented insights into the elementary steps of the hydrogenation and pinacol-coupling reactions of a ketyl species. In contrast to the successful isolation and structural characterization of fluorenone ketyl complexes, the similar reactions of the lanthanide reducing agents with benzophenone did not afford a structurally characterizable benzophenone ketyl species, and in some cases yielded the corresponding hydrogen abstraction products (e.g., **2**). These results show that benzophenone ketyl is less stable and more reactive than fluorenone ketyl, which is probably due to the less conjugated structure of benzophenone ketyl.[10] Very recently, it was reported that the use of Na/HMPA,[38] Ca/HMPA,[10] and samarium(II) bis(hydrotris(3,5-dimethylpyrazolyl)borate)[13] as reducing agents in the reaction with benzophenone had afforded the corresponding structurally characterizable benzophenone ketyl complexes. These results again demonstrate that the choice of reducing agents including metals and ancillary ligands is extremely crucial for the isolation of a ketyl species. It is obvious from the data presented in this paper and those previously[9,10,12,13] that trapping of a ketyl species in the coordination spheres of metals with appropriate ancillary ligands could constitute a useful method for the stabilization, isolation, and control of the reactivity of ketyl radicals.

Experimental Section

General Methods. All manipulations were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an Mbraun glovebox. The argon was purified by passing through a Dryclean column (4A molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4A) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure both were always below 1 ppm. Samples for spectroscopic studies were prepared in the glovebox. J. Young valve UV cells and NMR tubes (Wilmad 528-JY) were used for measurements. UV−vis spectra were recorded on a Hitachi 330 spectrometer, and the cell temperature was calibrated by using a Cu/constantan thermocouple in the case of variable-temperature measurements. ESR spectra were obtained on a JEOL JES FE 3AX X-band spectrometer, and the *g* values were calibrated with DPPH (2,2-diphenyl-1-picrylhydrazyl). ^{1}H NMR spectra were measured on a JNM-EX 270 (FT, 270 MHz) spectrometer and are reported in parts per million downfield from tetramethylsilane. Elemental analyses were performed by the chemical analysis laboratory of The Institute of Physical and Chemical Research (RIKEN). Tetrahydrofuran (THF), diethyl ether, benzene, toluene, and hexane were distilled from sodium/benzophenone ketyl, degassed by the freeze−thaw method (three times), and dried over fresh Na chips in the glovebox. Hexamethylphosphoric triamide (HMPA) was distilled from Na under reduced pressure, degassed by the freeze−thaw method (three times), and dried over molecular sieves (4A). Deuterated solvents (C_6D_6 and THF-d_8) were purchased from ISOTEC Inc., degassed by the freeze−thaw method (three times), and dried over fresh Na chips in the glovebox. Benzophenone and fluorenone were purchased from Tokyo Kasei Co. and recrystallized from MeOH. Samarium and ytterbium metals (40

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[38] Hou, Z.; Jia, X.; Wakatsuki. Y. Unpublished results. See also ref 12.

mesh) were obtained from Shiga Rare Metallic Co. Sm(N(SiMe$_3$)$_2$)$_2$(THF)$_2$,[30] Sm(OAr)$_2$(THF)$_3$ (**1a**),[15b] (C$_5$Me$_5$)$_2$Ln(THF)$_2$ (Ln = Sm,[28] Yb[29]), and (C$_5$Me$_5$)Sm(OAr)(HMPA)$_2$ [15a] were prepared according to the literature. Yb(OAr)$_2$(THF)$_3$[15b,16] (**1b**) and Yb(N(SiMe$_3$)$_2$)$_2$(THF)$_2$[8,39] were synthesized similarly to their Sm analogues. Ln(OAr)$_2$(HMPA)$_2$ (**1c**: Ln = Sm, **1d**: Ln = Yb[15c,e]) were synthesized by reactions of **1a,b** with 2 equiv of HMPA in THF.[40] Sm(N(SiMe$_3$)$_2$)$_3$[32] was prepared by reaction of SmI$_3$ with 3 equiv of NaN(SiMe$_3$)$_2$ in THF. The UV−vis spectroscopic data for ketyl complexes are summarized in Table 3.

Yb(OCHPh$_2$)$_2$(OAr)(HMPA)$_2$ (2). To 204 mg of Yb(OAr)$_2$(HMPA)$_2$ (**1d**) (0.21 mmol) in THF (3 mL) was added a THF solution of benzophenone (38 mg, 0.21 mmol) at room temperature. The color of the mixture turned immediately from orange to blue. After being stirred for 4 h, the solvent was evaporated to give blue fine (sheet-shaped) crystals. Attempts to recrystallize these crystals from THF/benzene, gave after a few weeks colorless blocks of **2** (77 mg, 0.07 mmol, 66% yield based on benzophenone (33% based on **1d**)). Anal. Calcd for C$_{53}$H$_{81}$N$_6$O$_5$P$_2$Yb: C, 56.98; H, 7.31; N, 7.52. Found: C, 57.24; H, 7.31; N, 7.42.

Sm(biphenyl-2,2′-diyl ketyl)(OAr)$_2$(THF)$_3$ (3a). Addition of a THF solution (2 mL) of fluorenone (180 mg, 1 mmol) to a THF solution (3 mL) of Sm(OAr)$_2$(THF)$_3$ (**1a**) (806 mg, 1 mmol) generated immediately a purple-brown solution. The mixture was stirred at room temperature for 4 h, and the solvent was evaporated to give a purple-brown crystalline product, which after recrystallization from THF/benzene gave **3a** as purple-brown blocks (804 mg, 0.88 mmol, 88% yield). Anal. Calcd for C$_{51}$H$_{70}$O$_5$Sm: C, 67.06; H, 7.72. Found: C, 66.73; H, 7.81.

Hydrolysis of 3a. Addition of 2 N HCl to a purple-brown THF solution (5 mL) of **3a** (228 mg, 0.25 mmol) under an argon atmosphere gave immediately a yellow mixture, which was extracted with ether (3 × 30 mL) and dried over Na$_2$SO$_4$. After filtration and evaporation of the solvent, a crude product was obtained as a white solid (155 mg), which was confirmed to be a 4:1 mixture of ArOH (0.50 mmol) and **4** (0.125 mmol) by ^{1}H NMR comparison with authentic samples. Attempts to separate them were not made.

Air Oxidation of 3a. Upon exposure to the air with stirring, a purple-brown THF solution (5 mL) of **3a** (228 mg, 0.25 mmol) changed immediately to a yellow solution. After hydrolysis and extraction with ether as described above, a crude product was obtained as a yellow solid (150 mg), which was confirmed to be a 2:1 mixture of ArOH (0.48 mmol) and fluorenone (0.24 mmol) by ^{1}H NMR comparison with authentic samples. A trace amount of fluorenol was also observed.

Reaction of 3a with 1a. To a purple-brown THF solution (5 mL) of **3a** (228 mg, 0.25 mmol) was added a brown THF solution (5 mL) of **1a** (202 mg, 0.25 mmol). The mixture was stirred at room temperature overnight, and a THF-insoluble purple precipitate was gradually formed. After hydrolysis and extraction with ether as described above, a crude product was obtained as a white solid (265 mg), which was confirmed to be a 4:1 mixture of ArOH (1.0 mmol) and fluorenol (0.25 mmol) by ^{1}H NMR comparison with authentic samples.

Yb(biphenyl-2,2′-diyl ketyl)(OAr)$_2$(THF)$_3$ (3b). Complex **3b** was obtained as brown blocks in 85% yield by reaction of Yb(OAr)$_2$(THF)$_3$ (**1b**) with fluorenone similarly to **3a**. Anal. Calcd for C$_{51}$H$_{70}$O$_5$Yb: C, 65.43; H, 7.54. Found: C, 65.20; H, 7.37.

Sm(biphenyl-2,2′-diyl ketyl)(OAr)$_2$(HMPA)$_2$ (3c). Complex **3c** was obtained as dark-green blocks in 90% yield by reaction of Sm(OAr)$_2$(HMPA)$_2$ (**1c**) with fluorenone similarly to **3a**. Reaction of **3a** with 2 equiv of HMPA in THF also afforded **3c**. Anal. Calcd for C$_{55}$H$_{90}$N$_6$P$_2$O$_5$Sm: C, 58.58; H, 8.04; N, 7.45. Found: C, 57.84; H, 7.88; N, 7.18.

Yb(biphenyl-2,2′-diyl ketyl)(OAr)$_2$(HMPA)$_2$ (3d). Complex **3d** was obtained as dark-green blocks in 86% yield by reaction of Yb(OAr)$_2$(HMPA)$_2$ (**1d**) with fluorenone similarly to **3a**. Reaction of **3b** with 2 equiv of HMPA in THF also afforded **3d**. Anal. Calcd for C$_{55}$H$_{90}$O$_5$N$_6$P$_2$Yb: C, 57.43; H, 7.89, N; 7.31. Found: C, 57.33; H, 7.62; N, 7.41.

(C$_5$Me$_5$)$_2$Sm(biphenyl-2,2′-diyl ketyl)(THF) (3e). To a purple THF solution (20 mL) of (C$_5$Me$_5$)$_2$Sm(THF)$_2$ (564 mg, 1 mmol) was added fluorenone (180 mg, 1 mmol) in THF (10 mL). The resulting dark-green solution was stirred at room temperature for 2 h, and the solvent was evaporated to give a dark-green crystalline product. The product was dissolved in toluene to give a dark-green solution which after concentration under reduced pressure yielded **3e** as dark-green blocks (478 mg, 0.71 mmol, 71% yield). A second crop (108 mg, 0.16 mmol, 16% yield) was obtained by slow concentration of the mother liquor. Anal. Calcd for C$_{37}$H$_{46}$O$_2$Sm: C, 66.02; H, 6.89. Found: C, 65.61; H, 7.01.

(C$_5$Me$_5$)$_2$Yb(biphenyl-2,2′-diyl ketyl)(THF) (3f). Complex **3f** was obtained as dark-green fine crystals in 85% yield by the similar reaction of (C$_5$Me$_5$)$_2$Yb(THF)$_2$ with fluorenone. Anal. Calcd for C$_{37}$H$_{46}$O$_2$Yb: C, 63.87; H, 6.66. Found: C, 63.43; H, 6.71.

(C$_5$Me$_5$)$_2$Sm(biphenyl-2,2′-diyl ketyl)(HMPA) (3g). HMPA (0.174 mL, 1 mmol) was added to a reaction mixture of (C$_5$Me$_5$)$_2$Sm(THF)$_2$ (564 mg, 1 mmol) and fluorenone (180 mg, 1 mmol) in THF (30 mL). The dark-green solution was stirred at room temperature for 1 h, and was slowly concentrated under reduced pressure to yield dark-green crystals of **3g** (663 mg, 0.85 mmol, 85% yield). Reaction of **3e** with 1 equiv of HMPA in THF also afforded **3g**. Anal. Calcd for C$_{36}$H$_{56}$O$_2$N$_3$PSm: C, 60.03; H, 7.23; N, 5.39. Found: 59.76; H, 7.31.

(C$_5$Me$_5$)$_2$Yb(biphenyl-2,2′-diyl ketyl)(HMPA) (3h). Addition of HMPA (0.174 mL, 1 mmol) to a dark-green reaction mixture of (C$_5$Me$_5$)$_2$Yb(THF)$_2$ (587.6 mg, 1 mmol) and fluorenone (180 mg, 1 mmol) in THF (30 mL) gave a dark-brown solution, which was stirred at room temperature for 1 h. Evaporation of the solvent yielded a dark brown crystalline product. Recrystallization of this product from THF/hexane afforded **3h** as dark-brown crystals (691 mg, 86% yield). Reaction of **3f** with 1 equiv of HMPA in THF also afforded **3h**. Anal. Calcd for C$_{39}$H$_{56}$O$_2$N$_3$PYb: C, 58.34; H, 7.03; N, 5.23. Found: C, 57.12; H, 7.16; N, 5.37.

(C$_5$Me$_5$)Sm(OAr)(biphenyl-2,2′-diyl ketyl)(HMPA) (3i). To a dark-brown THF solution (20 mL) of (C$_5$Me$_5$)Sm(OAr)(HMPA)$_2$ (863.4 mg, 1 mmol) was added fluorenone (180 mg, 1 mmol) in 10 mL of THF. The resulting dark-green solution was stirred at room temperature for 3 h. After reduction of the solution volume under reduced pressure, hexane was layered to precipitate **3i** as dark-brown blocks (786 mg, 0.91 mmol, 91% yield). Anal. Calcd for C$_{44}$H$_{64}$O$_3$N$_3$PSm: C, 61.14; H, 7.46; N, 4.86. Found: C, 60.61; H, 7.45; N, 4.85.

[Sm(OAr)$_2$(OEt$_2$)]$_2$[1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diolate] (5a). Complex **3a** (229 mg, 0.25 mmol) was dissolved in hexane (20 mL) to give a light-brown solution, which after evaporation under vacuum, yielded a pale-yellow powder. This powder was dissolved in hexane to give a light-yellow solution, and the volume of the solution was reduced under vacuum. A few drops of diethyl ether were layered, and light-yellow crystals of **5a** (40 mg, 0.024 mmol) were deposited after 2 days. Dissolving the pale-yellow powder or **5a** in THF gave **3a** quantitatively. Anal. Calcd for C$_{94}$H$_{128}$O$_8$Sm$_2$: C, 66.93; H, 7.65. Found: C, 66.38; H, 7.42.

[Sm(N(SiMe$_3$)$_2$)$_2$(THF)]$_2$[1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diolate] (5b). To a purple-brown THF solution (10 mL) of Sm(N(SiMe$_3$)$_2$)$_2$(THF)$_2$ (616 mg, 1 mmol) was added fluorenone (180 mg, 1 mmol) in 10 mL of THF. The resulting brown solution was stirred at room temperature for 4 h. Slow concentration of the brown solution under reduced pressure yielded light-yellow crystals of **5b** (572.8 mg, 79% yield). ^{1}H NMR (C$_6$D$_6$, 22 °C) δ 7.30−8.30 (m, 16 H, fluorenyl), 2.85 (br s, 8 H, THF), −1.31 (br s, 8 H, THF), −2.25 (br s, 72 H, SiMe). Anal. Calcd for C$_{58}$H$_{104}$N$_4$O$_4$Si$_8$Sm$_2$: C, 48.14; H, 7.24; N, 3.87. Found: C, 47.74; H, 7.10; N, 3.56.

Sm(N(SiMe$_3$)$_2$)$_2$(biphenyl-2,2′-diyl ketyl)(HMPA)$_2$ (3k) and [Sm(N(SiMe$_3$)$_2$)$_2$(HMPA)]$_2$[(1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diolate)] (5c). Complex **5b** (290 mg, 0.2 mmol) was dissolved in 10 mL of THF to give a brown solution. Addition of HMPA (0.14 mL, 0.8 mmol) yielded a dark-green solution which was stirred at room temperature for 1 h. Concentration of the solution under reduced pressure afforded a mixture of dark-green crystals of **3k** (ca. 200 mg, 50% yield) and light-yellow crystals of **5c** (ca. 65 mg, 20% yield). A

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(39) ^{1}H NMR for Yb(N(SiMe$_3$)$_2$)$_2$(THF)$_2$ (C$_6$D$_6$, 22 °C): δ 3.54 (br s, 8 H, THF), 1.28 (br s, 8 H, THF), 0.40 (s, 36 H, NMe).

(40) Sm(OAr)$_2$(HMPA)$_2$ was confirmed to be isomorphous and isostructural with Yb(OAr)$_2$(HMPA)$_2$.[15c,e]

Table 10. Summary of Crystallographic Data

	2·C_6H_6	**3a**·C_6H_6	**3b**	**3c**·3C_4H_8O	**3e**	**3h**·C_6H_6	**3i**	**3k**	**5a**·C_6H_{14}	**5c**	**6**	**7a**	**7b**
formula	$C_{59}H_{87}N_6O_5P_2Yb$	$C_{57}H_{76}O_5Sm$	$C_{55}H_{78}O_6Yb$	$C_{67}H_{114}N_6O_8P_2Sm$	$C_{37}H_{46}O_2Sm$	$C_{45}H_{62}N_3O_2PSm$	$C_{44}H_{64}N_3O_3PSm$	$C_{37}H_{80}N_8O_3Si_4P_2Sm$	$C_{100}H_{142}O_8Sm_2$	$C_{62}H_{124}N_{10}O_4Si_8P_2Sm_2$	$C_{90}H_{86}N_6O_8P_2Sm_2$	$C_{57}H_{78}N_9O_6P_3Sm$	$C_{57}H_{78}N_9O_6P_3Yb$
FW	1195.38	991.64	1008.27	1343.98	673.18	881.03	864.39	1009.79	1772.94	1661.18	1742.47	1228.64	1251.28
cryst syst	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	Pn (no. 7)	$P2_1$ (no. 4)	$P2_1/n$ (no. 14)	$P2_1/a$ (no. 14)	$P2_1/a$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$P2_1/a$(no. 14)	$P2_1/a$ (no. 14)
a (Å)	23.237(5)	13.326(2)	13.297(1)	19.695(98)	10.923(4)	24.363(6)	28.162(9)	28.778(7)	13.011(2)	11.925(5)	25.605(7)	18.254(3)	18.228(2)
b (Å)	16.162(1)	19.651(3)	19.492(3)	15.052(8)	16.410(7)	17.273(4)	12.499(5)	14.982(3)	17.543(3)	11.962(2)	14.037(4)	23.970(5)	23.771(3)
c (Å)	17.966(4)	10.705(1)	10.687(2)	12.824(8)	9.083(3)	10.195(3)	12.493(4)	12.372(4)	12.191(2)	18.165(4)	25.884(8)	14.245(3)	14.151(2)
α (deg)		102.22(1)	102.36(1)						97.00(1)	90.11(2)			
β (deg)	112.10(1)	101.87(1)	102.24(1)	104.53(4)	97.06(3)	93.46(2)	94.40(3)	94.54(2)	111.74(1)	109.01(3)	109.37(2)	92.79(2)	92.72(1)
γ (deg)		103.34(1)	103.24(1)						108.06(1)	117.25(2)			
V (Å^3)	6251(2)	2570(1)	2533(1)	3685(3)	1616(1)	4282(2)	4384(3)	5317(2)	2367(1)	2143(1)	8777(4)	6226(2)	6124(1)
Z	4	2	2	2	2	4	4	4	1	1	4	4	4
D_c (g cm^{-3})	1.27	1.28	1.32	1.21	1.38	1.37	1.31	1.26	1.24	1.29	1.32	1.31	1.36
radiation, λ (Å)	Cu Kα, 1.541 84	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
data collcd	$\pm h, +k, +l$	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$	$\pm h, +k, +l$	$\pm h, -k, +l$	$\pm h, -k, +l$	$\pm h, -k, +l$	$\pm h, -k, +l$	$\pm h, \pm k, +l$	$+h, \pm k, \pm l$	$\pm h, +k, +l$	$\pm h, -k, +l$	$+h, +k, \pm l$
scan speed (deg/min)	8	8	6	6	6	6	6	6	8	6	6	6	6
2θ range (deg)	4−136	4−55	3−55	3−55	3−55	3−55	3−55	3−55	4−55	3−55	3−55	3−55	3−55
μ (cm^{-1})	36.473	11.889	18.854	8.791	18.414	22.338	14.094	12.925	12.815	15.511	15.026	10.723	16.503
no. of reflns collcd	11 586	12 483	11 754	7374	4218	9837	11 344	12 204	11 489	9862	8538	15 706	15 311
no. of reflns with $F_o \geq 5\sigma(F_o)$	9241	9935	10 276^a	4860^a	3438^a	6240^a	5940^a	6047^a	9137	6749^a	2924^a	6101^a	7737^a
no. of variables	667	617	559	660	360	469	469	496	497	397	491	685	685
R_{int}	0.05	0.03	0.02	0.05	0.02	0.06	0.05	0.05	0.04	0.03	0.05	0.06	0.05
R (%)	6.45	4.04	3.90	6.21	4.11	5.46	5.03	8.91	4.34	4.59	5.64	5.35	4.42
Rw (%)	7.35	5.10	4.96	8.54	5.20	7.06	6.52	11.05	5.36	5.62	7.85	6.40	6.43

[a] Number of reflections with $I_o \geq 3\sigma(I_o)$.

complete separation of **3k** from **5c** was difficult, but single crystals of both complexes suitable for diffraction studies were selected under a microscope. Reaction of $Sm(N(SiMe_3)_2)_2(THF)_2$ with 1 equiv of fluorenone and 2 equiv of HMPA in THF gave a similar result.

[Sm(fluorenoxy)(1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diolate)(HMPA)]$_2$ (6). To a light-yellow THF solution (5 mL) of $Sm(N(SiMe_3)_2)_3$ (474 mg, 0.75 mmol) and HMPA (0.13 mL, 0.75 mmol) was added a THF solution (5 mL) of **4** (140 mg, 1.49 mmol). The resulting dark-green solution was stirred at room temperature overnight, during which the color of the solution gradually faded. After reduction of the solution volume under reduced pressure and addition of ether, light-yellow crystals of **6** (536 mg, 0.31 mmol, 82% yield) were precipitated. ^1H NMR (THF-d_8) δ 7.80−6.80 (m, 48 H, fluorenyl), 5.43 (s, 2H, CH), 2.57 (d, $J = 8.0$ Hz, 36 H, NMe). Anal. Calcd for $C_{90}H_{86}N_6O_8P_2Sm_2$: C, 62.04; H, 4.97; N, 4.87. Found: C, 61.37; H, 4.88; N, 4.65.

Sm(biphenyl-2,2′-diyl ketyl)$_3$(HMPA)$_3$ (7a). Samarium metal powder (0.30 g, 2 mmol) was stirred with ICH_2CH_2I (2%) in 2 mL of THF for 1 h to activate the metal surface. Addition of HMPA (1.06 mL, 6.1 mmol) to this blue suspension gave immediately a purple mixture to which a THF solution (10 mL) of fluorenone (1.08 g, 6 mmol) was added. The resulting dark-green mixture was stirred at room temperature overnight and was filtered through a frit. Reduction of the solution volume under vacuum and addition of ether precipitated **7a** (1.60 g, 1.3 mmol, 65% yield) as dark-green blocks. ESR (in THF or solid, +20 to −170 °C) $g = 2.0027$. Anal. Calcd for $C_{57}H_{78}N_9O_6P_3Sm$: C, 55.72; H, 6.40; N, 10.26. Found: C, 56.10; H, 6.29; N, 10.27.

Yb(biphenyl-2,2′-diyl ketyl)$_3$(HMPA)$_3$ (7b). Complex **7b** was obtained as dark-green blocks in 60% yield by the similar reaction of Yb metal with 3 equiv of fluorenone. ESR (in THF or solid, +20 to −170 °C) $g = 2.0029$. Anal. Calcd for $C_{57}H_{78}N_9O_6P_3Yb$: C, 54.72; H, 6.28; N, 10.07. Found: C, 54.34; H, 6.10; N, 10.18.

Hydrolysis of 7a,b. These reactions were carried out in a way similar to that in the case of **3a**. The diol **4** was isolated in 98% yield.

Reaction of 7a with 4 or Benzopinacol. To a dark-green THF solution (5 mL) of **7a** (246 mg, 0.2 mmol) was added a THF solution (3 mL) of **4** (36 mg, 0.1 mmol). The mixture was stirred at room temperature overnight, and a green-yellow solution was finally formed. After reduction of the solution volume under reduced pressure and addition of ether, light-yellow crystals of **6** (105 mg, 0.06 mmol, 60% yield) were precipitated. Fluorenone was confirmed in the mother liquor by ^1H NMR comparison with an authentic sample. The similar reaction of **7a** with benzopinacol also afforded **6** in 62% isolated yield, and benzophenone was confirmed in the mother liquor.

X-ray Crystallographic Studies. Crystals for X-ray analyses were obtained as described in the preparations. The crystals were manipulated in the glovebox under a microscope mounted on the glovebox window, and were sealed in thin-walled glass capillaries. Data collections were performed at 20 °C on an Enraf-Nonius CAD4 diffractometer with a rotating anode (Cu Kα radiation, $\lambda = 1.541\,84$ Å, graphite monochromator, ω scan) for **2,** an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å, graphite monochromator, ω scan) for **3a** and **5a**, and a Mac Science MXC3K diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å, graphite monochromator, $\omega-2\theta$ scan) for **3b−e,h,i,k, 5b,c, 6,** and **7a,b**. Lattice constants and orientation matrixes were obtained by least-squares refinement of 25 reflections with $60° \le 2\theta \le 70°$ for **2**, and with $30° \le 2\theta \le 35°$ for **3a−e,h,i,k, 5a−c, 6,** and **7a,b**. Three reflections were monitored periodically as a check for crystal decomposition or movement, and no significant decay was observed. All data were corrected for X-ray absorption effects. The observed systematic absences were consistent with the space groups given in Table 10. Complexes **2, 3a,** and **5a** were solved by the UNICS-III program,[41] and **3b−e,h,i,k, 5b,c, 6,** and **7a,b** were solved by direct methods using SIR92 in the Crystan-GM software package. Hydrogen atoms were either located from the difference Fourier maps, or placed at calculated positions. Refinements were performed anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms by the block-diagonal least-squares method. The function minimized in the least-squares refinements was $\sum(|F_o| - |F_c|)^2$. Neutral atomic scattering factors were taken from the *International Tables for X-ray Crystallography*.[42] The residual electron densities were of no chemical significance. Crystal data and data collection and processing parameters are given in Table 10.

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Supporting Information Available: A listing of atomic coordinates, thermal parameters, and bond distances and angles for **2, 3a−c,e,h,i,k, 5a,c, 6,** and **7a,b** (70 pages). See any current masthead page for ordering and Internet access instructions.

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[41] Sakurai, T.; Kobayashi, K. *Rikagaku kenkyusho Hokoku* **1979**, *55*, 69.

[42] Cromer, D. T.; Waber, J. T. *International Tables for X.-ray Crystallography*; Kynoch: Birmingham, England, 1974.